

Naturally Occurring and Mining-Affected Dissolved Metals in Two Subbasins of the Upper Animas River Basin, Southwestern Colorado

The Upper Animas River Basin is a mineralized region of the San Juan Mountains in southwestern Colorado (fig. 1). The mining of gold, silver, and other metals has occurred in the region from the late 1800's through the present (1995). Efforts are being made to assess the effects of mining on water quality in the Upper Animas River Basin. However, naturally occurring concentrations of metals also can affect water quality (Runnells and others, 1992). Remediation goals for possible cleanup of abandoned mine lands need to consider the presence of natural dissolved metals. The U.S. Geological Survey, in cooperation with the Colorado Department of Public Health and Environment, is determining the concentrations of natural dissolved metals in the hydrologic system, as compared to metals from the effects of mining, in the Upper Animas River Basin.

The purposes of this fact sheet are to:

(1) Describe the methods of collection and analysis for water samples from selected subbasins of the Upper Animas River Basin; (2) describe the concentrations, loads, and attenuation of selected dissolved metals in two subbasins—Topeka and Ohio Gulches—of the Upper Animas River Basin (fig. 1); and (3) describe methods for tracing natural dissolved metals and present oxygen-isotope data for dissolved sulfate in water from natural and mining-affected sources.

Sample Collection and Analytical Methods

Water samples were collected from natural springs and streams (springs and streams determined to be unaffected by mining through hydrologic reconnaissance) in Topeka Gulch (fig. 1). Water samples also were collected from the drainage of two collapsed mines in Topeka Gulch and three mines in Ohio Gulch (fig. 1). Two mines in Ohio Gulch were sampled at the draining adits, and one was sampled in the receiving stream below several collapsed mines. Cement Creek was sampled at

the streamflow-gaging station (fig. 1). Water samples were filtered through a 0.45-micrometer (μm) filter (the term *dissolved* in this case is operationally defined as the solution that passes through a 0.45- μm filter). Water properties measured at each site were: pH, specific conductance, dissolved oxygen, alkalinity (if pH was greater than about 4.5), and water temperature. Discharge was measured at each site. Water samples were collected during the low-flow, late-summer period of September–October 1994 to minimize the effects of snowmelt on spring discharges. Water-chemistry analyses included: dissolved major ions, dissolved major and trace metals, sulfur isotopes of dissolved sulfate ($\delta^{34}\text{S}_{\text{SO}_4^{2-}}$), oxygen isotopes of dissolved sulfate ($\delta^{18}\text{O}_{\text{SO}_4^{2-}}$), oxygen isotopes of water ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$), and hydrogen isotopes of water ($\delta\text{H}_{\text{H}_2\text{O}}$). Cations were determined by inductively

coupled plasma spectrometry (ICP), and anions were determined by ion chromatography (IC). Dissolved metals were determined by ICP-mass spectrometry (ICP-MS). Isotopes were determined by isotope-ratio mass spectrometry (MS).

Samples collected from each site were analyzed for dissolved ferrous iron (Fe^{2+}), dissolved iron ($\text{Fe}^{2+} + \text{Fe}^{3+}$), and dissolved sulfate using a portable field spectrophotometer. Ferrous iron degrades rapidly after collection; therefore, field spectrophotometer analyses were done within 8 hours of collection. Dissolved iron was analyzed on the spectrophotometer in order to calculate ferric iron (Fe^{3+} or dissolved iron minus Fe^{2+}); then the oxidation/reduction potentials were calculated from the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios if the concentrations of iron species were greater than about 10^{-6} moles per liter. Dissolved sulfate was analyzed on the

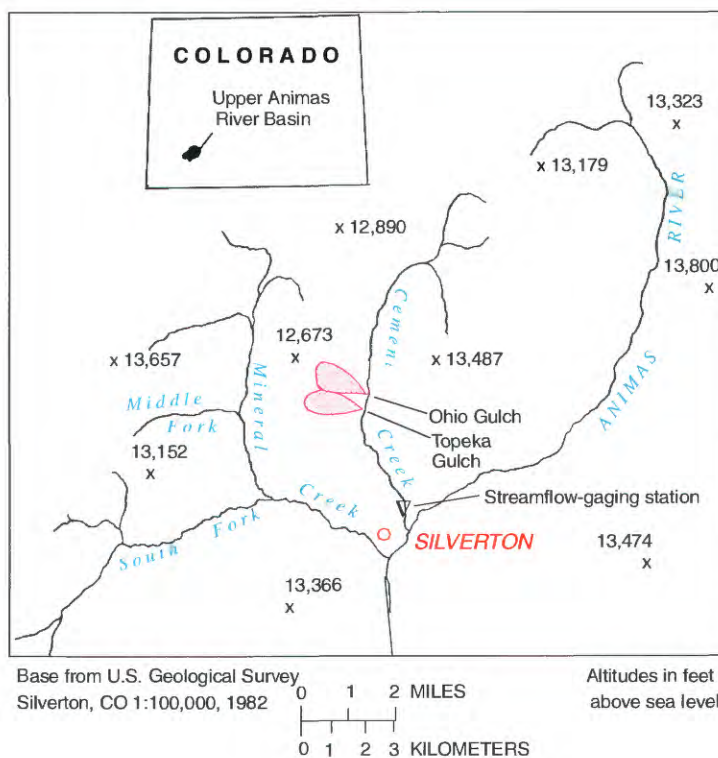


Figure 1. Location of Topeka Gulch, Ohio Gulch, and the streamflow-gaging station on Cement Creek, Upper Animas River Basin, southwestern Colorado.

spectrophotometer to estimate the amount of sulfate needed to pass through anion-exchange columns for shipment to the laboratory for $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ and $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ analyses.

Samples for analyses of $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ and $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ were collected on anion-exchange resin (chloride form) before sending to the laboratory. Calculated based on the sulfate spectrophotometer analysis, a measured amount of water was first passed through a chelating resin (sodium form) to remove iron because iron is an interferant to the $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ analysis; then the water was passed through an anion-exchange column sufficient to accumulate 80 milligrams (mg) of sulfate for the $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ analysis and 40 mg of sulfate for the $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ analysis. The anion-exchange columns were sent to the laboratory for extraction of the sulfate, and the chelating resins were disposed.

Naturally Occurring and Mining-Affected Dissolved Metals

In this fact sheet, natural and mining-affected concentrations and loads of aluminum, iron, and zinc in Topeka and Ohio Gulches will be discussed as the dissolved metals of concern because of their prevalence in streams of the Upper Animas River Basin. Complete water-chemistry analyses for water samples collected in the study area can be obtained upon request from the U.S. Geological Survey.

Concentrations

Concentrations of dissolved aluminum in natural springs, a natural stream, and mines in Topeka and Ohio Gulches ranged from 7 to 22,000 micrograms per liter ($\mu\text{g/L}$) (fig. 2), and concentrations of dissolved iron ranged from 3,600 to 78,000 $\mu\text{g/L}$ (fig. 2). Concentrations of dissolved zinc ranged from 6 to 7,440 $\mu\text{g/L}$ (fig. 3). Water from natural springs and streams had similar aluminum, iron, and zinc concentrations compared to water from mines in Topeka and Ohio Gulches.

Water from natural springs, a natural stream, and mines in Topeka and Ohio Gulches had pH values ranging from 2.84 (very acidic) to 6.95 (near neutral) (fig. 4). These acidic pH values of natural springs and streams indicate the oxidation of metal-sulfide minerals in the natural ground-water system, which is unaffected by mining.

Loads

During the sampling period, natural springs and streams contributed substantial dissolved metal loads (discharge times concentration) to Topeka Gulch. Dissolved aluminum and iron loads (fig. 5) were much larger than the dissolved zinc loads (fig. 6). Mines in Topeka and Ohio Gulches also contributed substantial dissolved aluminum, iron, and zinc loads (figs. 5 and 6).

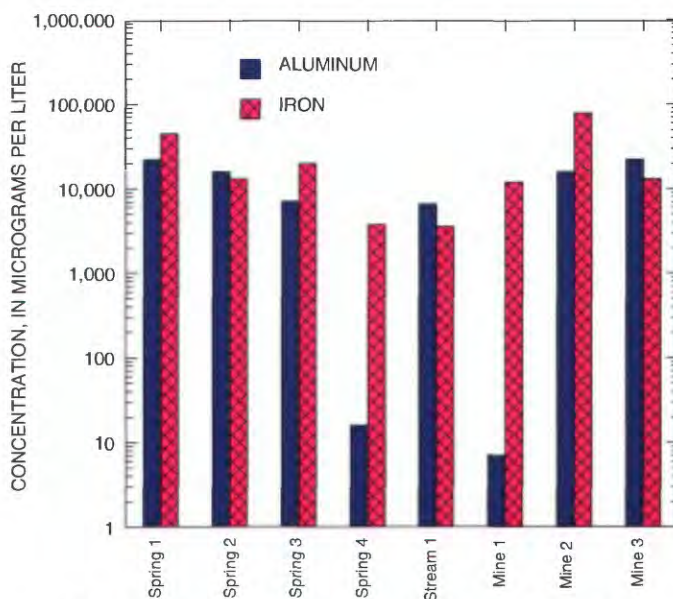


Figure 2. Concentrations of dissolved aluminum and iron in natural springs, a natural stream, and mines in Topeka and Ohio Gulches, Upper Animas River Basin.

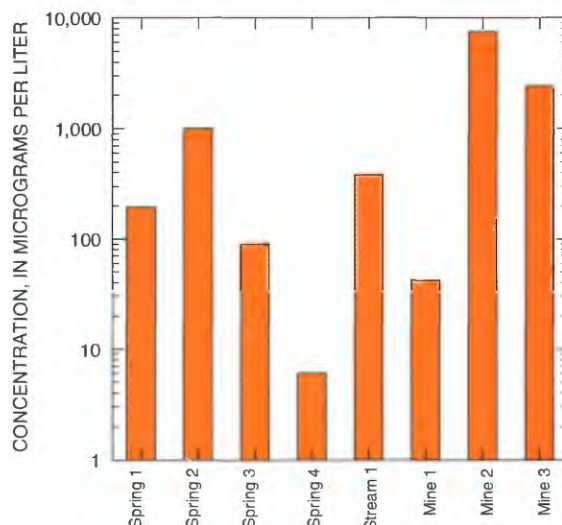


Figure 3. Concentrations of dissolved zinc in natural springs, a natural stream, and mines in Topeka and Ohio Gulches, Upper Animas River Basin.

Metals Attenuation

The concentrations of dissolved aluminum, iron, and zinc were lower (attenuated) at the mouth of Topeka Gulch compared to upper reaches. The metals could have been attenuated by natural adsorption processes by the stream water flowing in and out of the alluvial aquifer at the lower end of the gulch. Metals could be stored in the alluvium and possibly remobilized during high flows such as snowmelt runoff; however, this possibility was not analyzed and warrants further investigation.

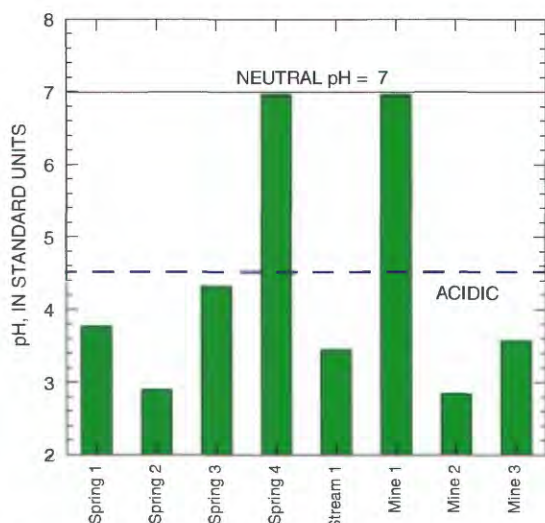


Figure 4. pH of water from natural springs, a natural stream, and mines in Topeka and Ohio Gulches, Upper Animas River Basin.

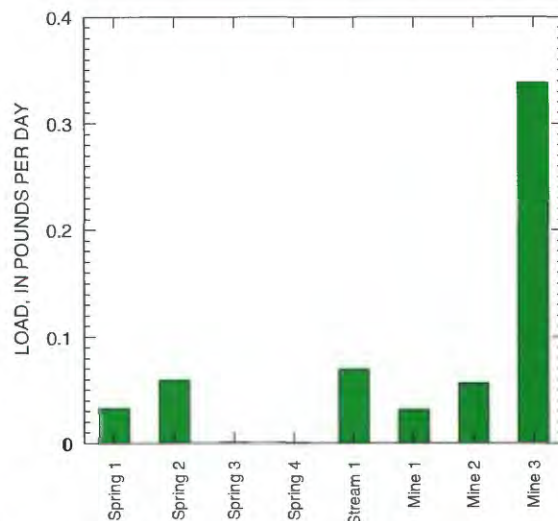


Figure 6. Dissolved zinc loads in natural springs, a natural stream, and mines in Topeka and Ohio Gulches, Upper Animas River Basin.

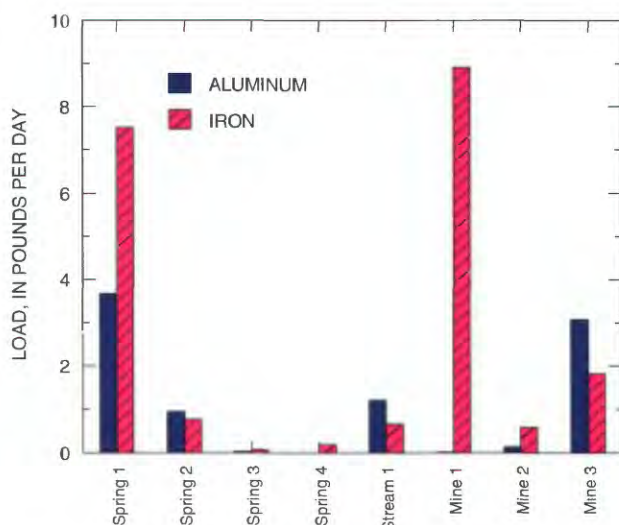


Figure 5. Dissolved aluminum and iron loads for natural springs, a natural stream, and mines in Topeka and Ohio Gulches, Upper Animas River Basin.

Tracers of Natural Dissolved Metals

Conservative Constituents

Naturally occurring dissolved metals can be traced by sampling water from natural springs and streams, analyzing for conservative constituents (constituents that remain dissolved in the water in contrast to constituents that might be attenuated by natural processes), and comparing natural dissolved metal loads to loads in the part of the stream that is affected by mining (Bencala and

others, 1987). This procedure was performed for Topeka Gulch; however, the analysis represents only a snapshot of the dissolved metals during the time period of sample collection. Barium and nickel seemed to act as conservative constituents in the study area.

Natural springs and streams in Topeka Gulch contributed 39 percent of the discharge, 51 percent of the barium load, and 40 percent of the nickel load to the mouth of Topeka Gulch. Mines in Topeka Gulch, therefore, contributed 49 percent of the dissolved barium load and 60 percent of the dissolved nickel load. At the streamflow-gaging station on Cement Creek (fig. 1), natural springs and streams in Topeka Gulch contributed 0.42 percent of the discharge, 0.73 percent of the barium load, and 0.47 percent of the nickel load.

Oxygen Isotopes of Dissolved Sulfate

In sulfide-mineralized geologic regions that have been mined, such as the Upper Animas River Basin, the oxidation of sulfide minerals produces dissolved sulfate in natural springs and in mine drainage. In some collapsed mines, the dissolved sulfate can be subject to microbial reduction. The oxygen in dissolved sulfate (SO_4^{2-}) can be affected by several processes: (1) Oxidation of sulfide minerals by oxygen in ground water (H_2O) that has low dissolved-oxygen concentrations (such as natural springs that have deep ground-water flow paths); (2) oxidation of sulfide minerals by atmospheric oxygen (O_2) in contact with the ore body (such as in an open mine); and (3) oxygen in dissolved sulfate where sulfide minerals were oxidized when water first enters the old mine, then part of the sulfate was subjected to reduction by sulfate-reducing bacteria because of the lack of atmospheric circulation to keep the system in an oxidizing condition.

Water samples from naturally occurring and mining-affected sources were analyzed for the oxygen-18/oxygen-16 stable isotope value of dissolved sulfate ($\delta^{18}\text{O}_{\text{SO}_4^{2-}}$). The $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ was related to the dissolved-sulfate concentration for each site (fig. 7) (Taylor and Wheeler, 1994). The figure indicates distinct groupings for the three processes affecting oxygen in dissolved sulfate described above. More data are needed to develop a clearer understanding of the ranges of $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ values in the Upper Animas River Basin so that mass-balance equations can be used to calculate the amount of natural constituents in streams.

Summary

Water from natural springs and streams in Topeka Gulch (a subbasin of the Upper Animas River Basin) had high concentrations of dissolved metals during the low-flow period of September–October 1994. Natural sources contributed substantial dissolved metal loads to the mouth of Topeka Gulch, and natural sources in Topeka Gulch contributed measurable dissolved metal loads to Cement Creek. Mines (open and collapsed) in Topeka and Ohio Gulches had similar concentrations and loads of dissolved metals compared to naturally occurring springs and streams in Topeka Gulch. The $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ isotope method indicated three distinct groupings for the sources of oxygen that contribute dissolved sulfate to streams in the area. The $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ isotope method has promise for estimating the percentage of natural dissolved metals in mainstem streams. However, more data are needed to establish a clearer understanding of $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ isotopes in the Upper Animas River Basin.

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For information and selected readings about the Upper Animas River Basin, write to:

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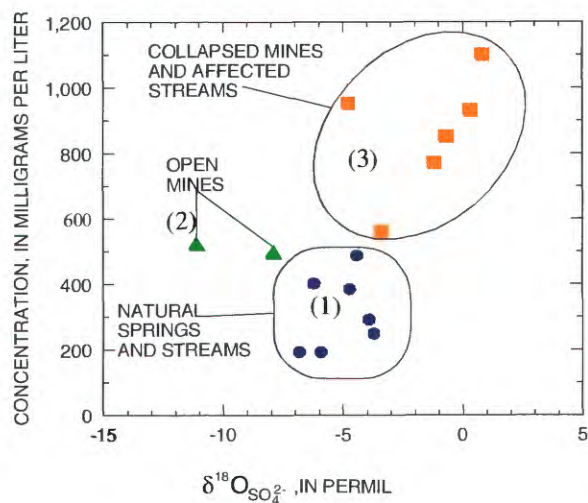


Figure 7. Relation between oxygen isotopes of dissolved sulfate and concentration of dissolved sulfate in water samples from Topeka Gulch, Ohio Gulch, and Cement Creek, Upper Animas River Basin.

References Cited

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